

Daniel Knez<sup>1</sup>, Christian Gspan<sup>2</sup>, Nikola Šimić<sup>2</sup>, Stefan Mitsche<sup>1,2</sup>, Harald Fitzek<sup>2</sup>,  
Gerald Kothleitner<sup>1,2</sup>, Werner Grogger<sup>1,2</sup>, Ferdinand Hofer<sup>1,2</sup>

<sup>1</sup> Institute of Electron Microscopy and Nanoanalysis, Graz University of Technology, Graz, Austria

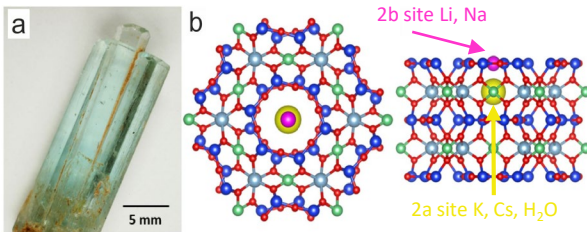
<sup>2</sup> Graz Centre for Electron Microscopy, Graz, Austria

## Introduction

Nanoporous materials are a large group of materials with a wide range of scientific and technical applications. Understanding the fundamental mechanisms of diffusion and adsorption of atomic and molecular species within the pores of this class of materials is, therefore, of paramount importance. While the localization of atoms and molecules in pores has already been demonstrated using high resolution TEM based techniques [1,2], a quantitative understanding is still missing. This is due to difficulties such as the lack of electron probe confinement [3], small focal depth and the high susceptibility of porous materials to electron beam damage.

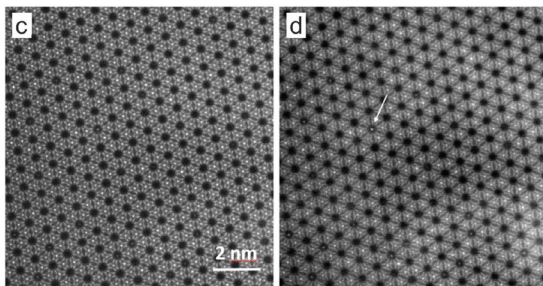
## The Beryl Structure

Beryl, ideally  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ , has a hexagonal crystal structure of space group  $P6/mcc$  with  $\text{AlO}_6$  octahedral and  $\text{SiO}_4$  tetrahedral forming a framework of well defined channels that can be occupied by various guest components; e.g. K, Cs and  $\text{H}_2\text{O}$  in the wider 2a sites (0.5 nm) and Li, Na in the smaller 2b sites (0.28 nm). We studied an aquamarine crystal with a low content of Cs and traces of Li and K. Fe and Sc were also observed, but they go to the octahedral site. Figure 1a) shows the crystal; b) crystal structure of beryl with Cs and Li ions in the channel cavity; Cs on site 2a (yellow) and Li on site 2b (magenta); top view and side view of the structure.



## Experimental Results

High-resolution STEM studies were performed with a probe-corrected Thermo Fisher Titan<sup>3</sup>, 300 kV, X-FEG and a convergence angle of 15 mrad, HAADF detector (angular range 48 to 242 mrad), ADF detector (18-67 mrad), CL= 91 mm. HAADF STEM image (c) viewed along the [001] direction and d) ADF STEM image showing some channels occupied by guest components.



## Acknowledgements

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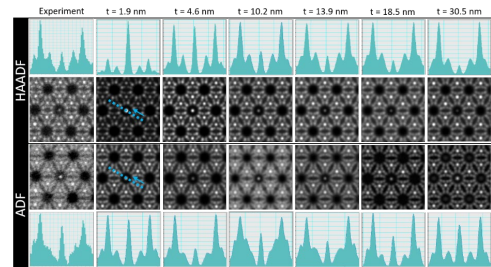
## Contact

daniel.knez@felmi-zfe.at

ferdinand.hofer@felmi-zfe.at

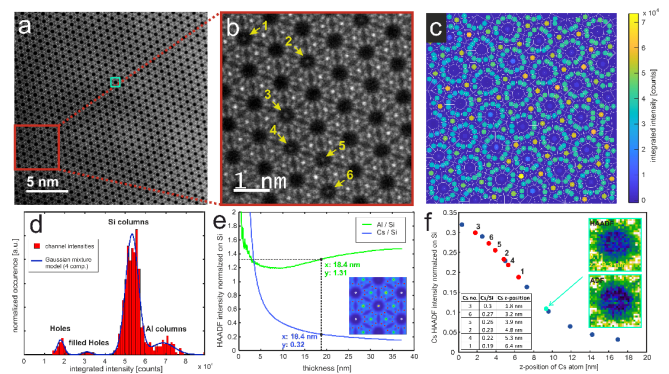
## HAADF-Simulations

Qualitative comparison of experimental STEM images of the brightest channel occupant to multi slice simulations with QSTEM viewed along the [001] direction; with the assumption of one Cs ion in the top position  $t = 0$  and for a specimen thickness range from  $t = 1.9$  nm to  $t = 30.5$  nm. The position of the intensity profile is highlighted by a blue dotted line and the same for every image. The arrow signifies the orientation of the profile.



## Quantitative Interpretation

Overview STEM HAADF image. (b) Magnified region highlighted in (a) containing 6 filled channels. (c) Quantitative analysis of the atomic columns via Voronoi tessellation and areal integration. (d) histogram of the intensities determined in (c). The different contributions and their mean are determined with a 4 component Gaussian mixture model. (e) Al/Si and Cs/Si intensity ratios over thickness obtained from multislice simulation series with one Cs atom at the topmost position of the channel, blue dots are extracted from simulations at fixed crystal thickness and red dots correspond to the experimental data with according numbering shown in (b). The inset representatively shows the experimental detection limit of a single Cs atom in the channel, identified in the region highlighted in (a).



## Conclusions

- Individual Cs atoms can be detected unambiguously.
- The position of the Cs atoms in the channels can be determined from a single HAADF image; by internal calibration with the Al/Si and Cs/Si intensity ratios.
- Cs atoms can only be detected in the upper part of the sample (experimental detection limit for HAADF is around 10 nm sample thickness).

## References

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- Kimoto et al., Appl. Phys. Lett. 94 (2009) 041908-1-3.

